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The Metallurgist.

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Polished Surfaces.

AT the Congress of the International Association for Testing Materials recently held in London, a section of the programme was devoted to the progress of metallography, and in this an important place was taken by discussions on the application of electron interference methods to the study of metals. It is just ten years ago since Davisson and Germer in America and G. P. Thomson and Reid in this country first demonstrated the diffraction of a stream of electrons, and both confirmed the predictions of De Broglie as to the relation between the kinetic energy of the electrons in the beam and the wave length of their associated wave systems, and at the same time established a new method of investigating atomic arrangement which was particularly suitable for the study of the surface layers of metals and other materials.

One of the earliest problems to which the new method was applied was the investigation of the nature of polish. When it was found that the sharp rings characteristic of the diffraction pattern given by crystalline materials gave place, when a metal was polished, to faint diffused halos similar to those obtained from the surface of liquid mercury, strong evidence was thought to have been obtained of the existence of an amorphous surface layer of the type postulated by Beilby. Professor F. Kirchner, of Cologne, showed, however, that minute surface irregularities, such as might remain if polishing consisted only of the rubbing away of surface projections, would be sufficient to account for the diffused character and lack of sharpness of the halos produced by diffraction of the electron beam. On the other hand, the amorphous theory found support from the work of Finch, Quarrell, and Roebuck, who in 1934 observed that a thin film of zinc deposited on a polished copper surface at first gave rise to a brilliant and well-defined electron diffraction pattern characteristic of crystalline zinc, but that this pattern quickly faded and disappeared completely after a few seconds, although zinc similarly deposited on a crystalline copper surface gave a diffraction pattern which remained unchanged for 1½ hours. The discovery of the remarkable solvent power of the surface layer of polished copper, not shown by the corresponding crystalline surface, strongly suggests the amorphous character of the polished surface.

It should be mentioned that Professor Kirchner, who also had a paper at the Congress, has apparently not been able to secure the requisite experimental conditions and has not confirmed the solution of zinc in the surface layers of polished copper at atmospheric temperature. Professor Finch agrees that it is not easy to demonstrate the solution of zinc crystals in the amorphous layer produced on copper by light hand polishing, but the effect is said to be readily observed when the polish has been produced by vigorous buffing.

A very interesting and informative account of these researches is given by Professor G. I. Finch in the current number of *Science Progress*, which in several recent issues has contained reviews of physical subjects of great interest to metallurgists. Both in this paper and in his communication to the International Congress, Professor Finch not only summarised the evidence for the Beilby layer on polished surfaces, but dealt with the application of the results of electron diffraction investigations to the interpretation of phenomena of wear and lubrication. For example, it has been found that when a smooth surface of cast iron of the quality used for making piston rings is lightly rubbed with a fine grade emery paper and then examined in the electron diffraction camera, a pattern of graphite is obtained and not, as might have been expected, one of iron crystals. The effect of even very fine abrasion is to cause the graphite inclusions to spread out over the surface in such a way as to act as a lubricant.

The tendency of the amorphous material to recrystallise is controlled by the orientation of the underlying crystals. This is discussed in more detail by Professor Finch in a paper on "The Nature of Polish," published in the "Transactions" of the Faraday Society for March, 1937. There it is shown experimentally that polishing results in flow on calcite single-crystal surfaces, and that the polish layer is crystalline and integral in structure with the underlying crystal when the surface is a cleavage plane or lies close in its direction to one of the cleavage planes, but that, on the other hand, it affords halo patterns when the polished surface is steeply inclined to all cleavage planes. Heating leads to the gradual emergence of a single crystal pattern, which eventually replaces the halo pattern. It is concluded that the crystalline structure of the polish layer on the calcite cleavage plane is due to recrystallisation of the amorphous material under the influence of the underlying crystal, an influence which, however, is weak in surfaces steeply inclined to the direction of cleavage.

A complete review of the subject was not possible in the short time available at the International Congress, but in his paper Professor Finch referred to the structure of electro-deposited metals. It is possible that electron diffraction methods applied to the initial stages of deposition of a film of electro-deposited metal may throw light on some of the problems of adhesion. Such a study must be linked up with a technique which makes full use of the already known methods of ensuring a high degree of adhesion of electro-deposited metals to the underlying surface.

The papers and discussion at the Congress fully

confirmed Professor Finch's concluding statement that "electron diffraction may be said to have already won a position for itself alongside X-rays and the microscope. Each covers its own field and each is complementary to the other; the realisation of the full advantages and powers of electron diffraction and of the older methods in advancing the science of metallography must lie in their future co-operation."

Theories of Age-Hardening.

A TRUE theory is also a "theorem"—a logical argument from one set of facts or assumptions to another—and in the realm of experimental science the criteria of a theory are its adequacy as a picture and its ability to lead to new observations. In the age-hardening field the original observation of Merica, Waltenburg, and Scott,[1] that in order to age-harden an alloy must first be brought to a state of thermodynamic instability, though rather obvious, was of great theoretical significance, since it limited the pursuit of possible age-hardening alloys to alloys lying in phase regions which become narrower or disappear entirely on change of temperature. This theory resulted in a burst of discovery of new age-hardening alloys, especially perhaps since it gave no support to the view then current that this phenomenon of age-hardening was to be sought only at or near the ordinary temperatures. On the other hand, the criteria advanced above are not satisfied by many "theories" advanced by metallurgists, who adopt the word "theory" when they refer to the description of a mechanism not completely defined by the experimental evidence, and this is particularly true of the two so-called theories of age-hardening, usually known as the precipitation theory and the knot theory. The precipitation theory relates high hardness values to the existence of discrete particles of a precipitated phase, and the knot theory associates the maximum hardness with a much earlier stage of the breakdown of the original unstable solid solution, when the solute atoms are still on the solvent lattice, but in a modified distribution. These "theories" are no more than vague generalised descriptions, each applying only to a limited number of alloys. The terms "precipitation hardening" and "knot hardening" have been useful as classifications, relating structure and hardness, but as any given alloy might well belong to either type, structural characteristics may not be used to infer its state of hardness; and so these "theories" lead nowhere.

It is interesting to consider from this standpoint the recent papers of Cohen,[2] of which an account has already been presented in THE METALLURGIST,[3] and of Gayler,[4] especially as in the discussion of the latter at the Spring Meeting of the Institute of Metals one speaker suggested that the hypothesis advanced was not rightly described as a theory. Cohen, it will be remembered, studied the age hardening of a copper-silver alloy, and reached the novel conclusion that this material is capable of exhibiting both knot hardening and true precipitation hardening effects. Dr. Gayler's paper contains a "general theory of age-hardening," based mainly on her previously published researches on light alloys and evidence taken from the papers of other workers. Her theory is completely independent of Cohen, but her views are practically identical with his. The "theory" briefly is this: All age-hardening alloys are both knot hardening and precipitation hardening alloys, and show two hardness peaks on their ageing curves, corresponding to these two stages, unless ageing is carried out at temperatures so low that the second stage is never entered or so high that the knot stage passes before it can be observed. According to this view, there is a very real difference between an alloy age-hardened at low and at high ageing temperatures (such as duralumin treated at room temperature and at 200 deg. Cent.), since at the low temperature true precipitation cannot occur, however prolonged the ageing, if only the first hardening stage is involved, whereas treating to or near the maximum hardness attainable at the high temperature involves true precipitation. In the specialised department of light alloys, this amounts to a detailed restatement of the view previously advanced by Meissner,[5] Gayler and Preston,[6] and others, that a "critical temperature" looms large in the heat treatment of duralumin, above and below which quite distinct mechanisms of age hardening apply, the one resulting in loss of ductility and increased susceptibility to corrosive attack, whilst the other is without adverse effects in these directions. Other workers have, however, suggested that this differentiation may be largely illusory, proceeding not directly from the changed temperature, but from the more complete ageing secured at high temperatures, and that the "critical temperature" of about 140 deg. Cent. is merely the lowest temperature at which maximum hardness is reached in a reasonable duration of exposure.[7] In this connection, it is interesting to note that the hardening curves given in Dr. Gayler's paper (Fig. 4) do not suggest a change in the mechanism of ageing between 100 deg. and 150 deg. Cent.

Dr. Gayler's argument demands implicitly that precipitation hardening alloys shall suffer, during their attempt to approach equilibrium, structural modifications which at one stage bring the alloy into the state in which knot hardening alloys are hard. On this point, both she and Cohen present clear evidence, Dr. Gayler citing her and Preston's observations and other facts from the literature, and Cohen producing new and definite X-ray data, together with dilatometric and electrical resistivity results, all indicating the knot stage. This evidence confirms the impression already shared by many workers in this field that the preliminaries to precipitation must run an almost parallel course in all alloys, independent of whether they exhibit knot hardening, precipitation hardening, both or neither. There is a general concensus of opinion that precipitation can occur only in a region of high supersaturation, so that the first stage must always be one which gathers solute atoms into groups. As the precipitated phase in alloys is usually rejected, not as randomly distributed spheres, but as regularly orientated plates or needles, in characteristic Widmannstätten patterns, many workers believe that the initial stages of diffusion set up an arrangement within the solution involving this type of segregation, rather than the more spherical grouping conveyed by the term "knot." It may be that only the earliest stages of diffusion are in the lattice proper and solute atoms soon become congregated on imperfection planes within the crystal, at which first slip normally occurs. It is unfortunate that the X-ray methods do not at present give a sufficiently precise answer to allow of the calculation of the early movements of the solute atoms, for if the accuracy of the picture presented above could be checked, the subject would be much advanced. Cohen's work brings out clearly the very important

point that the existence of the knot type of segregation does not necessarily imply marked hardening, as he observed the knot stage at temperatures at which there was no accompanying hardness curve inflection.

This being the case, one hesitates to accept Dr. Gayler's suggestion that two successive hardness peaks occur on all but a few age-hardening curves as the natural concomitants of the knot and precipitation stages. The evidence presented by Dr. Gayler on this point was referred to by Dr. Alexander, the speaker already quoted, as "unconvincing," as the deviation at the knot stage from a mean un-inflected curve is possibly within the limits of experimental error. Dr. Alexander, who has been studying age-hardening alloys for some years in the laboratory of Professor Hanson at Birmingham, has himself carried out a statistical examination of the age-hardening process, in which twenty hardness indents were made at each stage and the scatter as well as the mean values plotted against duration of ageing. In the resulting curves the maximum scatter was found in conjunction with an early inflection of the hardening curve which was therefore regarded as untrustworthy at this stage, presumably as the result of macroscopic non-uniformity of the progress of ageing.

Another speaker, Dr. Callendar, referred briefly to his work on the graphitic silicon content of aluminium alloys,[8] in which he found direct chemical evidence of precipitation at a much earlier stage than the microscope indicates during ageing at 200 deg. Cent. It may be remembered that Jenkins and Bucknall [7] have also drawn attention to early chemical evidence of precipitation in what is usually regarded as a knot hardening alloy, nickel-silicon-copper. The more recent X-ray examination of this material by Van Wert and Gonser,[9] although by no means positive, has, however, indicated that this is perhaps a precipitation hardening alloy. Fink and Smith have shown that in pure copper-aluminium alloys,[10] and more recently in magnesium-aluminium alloys,[11] there is microscopical evidence of precipitate at a stage when the lattice parameter is unchanged. It is thus becoming increasingly evident that the hardening of a material can only be assigned to either the knot or precipitation stage when a series of methods of examination indicate complete absence of precipitate at the stage of maximum hardness or the rejection by this time of every precipitable solute atom respectively. It is now certain that the two stages so defined do not include all those at which age-hardening alloys reach maximum hardness, and it seems likely that these structural stages are not themselves the cause of hardening. In this connection reference may be made to the views of Masing,[12] who has suggested that all the observed effects are secondary, arising from "disturbances" or strains set up during the ageing. It is, for example, sometimes argued that the maximum value of electrical resistivity frequently observed during ageing has no very precise structural significance, an opinion with which Dr. Gayler differs.

New light on this matter was shed by Professor Mott's contribution to the discussion, in which he said that on the wave-mechanical theory of electrical conductivity, a maximum resistivity is to be expected whenever the solute atoms in a solid metallic solution have become assembled into groups about five atoms across, even in the absence of cold working effects, which would, of course, also tend to increase the resistivity. In the theory the electrons which are "free" within the metal are pictured as waves with ascribed wave lengths around 5 atomic diameters. To the progress of such waves, *i.e.*, the passage of a current, individual solute atoms offer little interference, as also do scattered particles of comparatively large dimensions, yet groups of a few solute atoms are a decided hindrance. The analogy to the passage of light through an atmosphere containing water is complete. At a certain optimum particle size, which is comparable with the wave length of the light, the incident beam is scattered and cannot penetrate the fog; beyond this size raindrops offer progressively decreasing resistance to light. Why an initial rise of resistivity has only been observed with some age-hardening alloys is, however, a problem at present unsolved, but it is gratifying to know that a physicist of Professor Mott's standing is interesting himself in age-hardening and other metallurgical problems.

We have already referred briefly to the fact that in copper-silver alloys, according to Cohen's results, a particular structural configuration only implies hardening at certain ageing temperatures. In magnesium-aluminium alloys,[11] there is no change of mechanical properties at the knot stage, if this occurs, or even at the earliest stage of true precipitation, at which the grain boundaries are thickened by intergranular precipitate. Again, a dozen elements age harden copper slightly, yet two or three are able to cause the hardness to rise several hundred per cent., and similarly with other solvents different additions result in greatly varied degrees of age-hardening. It is here that lies the major problem in this field, one with which any successful theory must cope—the origin of the *specific* nature of the phenomenon. The work under review has served an extremely valuable purpose in exposing the weaknesses of the older methods of classifying age-hardening alloys, but if we are to find new and better materials, and this is surely the main goal of research work in this department of metallurgy, we must have the help of a more constructive theory, which deals with the alloys in which Merica and his co-workers indicated the possibility of age-hardening, and emphasises the differences between them, so leading to the recognition of the peculiarity of the original solution, other than mere thermodynamic instability, which is the predisposing cause of unusual hardenability.

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[10] Fink and Smith, "Metals Technology," June, 1936, A.I.M.E., T.P. 706.
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[12] Masing, discussing ref. 6.

The First International Electro-deposition Conference.

THE considerable activity which has been shown in the field of electro-deposition during the past ten or fifteen years has resulted in remarkable developments in the decoration of metals and in their protec-

tion from corrosion and wear, as well as in engineering applications, such as the building up of worn or undersized machine parts. The control of the process has changed from an empirical to a scientific basis, and it is now not only possible to deposit certain metals within defined limits of adhesion, structure, and mechanical properties, but also to produce coatings in practice whose protective value can be assessed by means of simple tests.

The First International Electro-deposition Conference, which was organised by the Electro-depositors' Technical Society, and held in London on March 3rd and 4th, provided an excellent opportunity for the exchange of information and views on the progress of knowledge and on the development of practice in various countries.

ELECTRO-DEPOSITION PRACTICE.

The opening session was devoted to a series of papers on electro-plating practice in America, France, Germany, Great Britain, and Russia. In general, little difference in essential principles was revealed with the exception that considerable attention appears to have been given in Russia to the development of acid solutions for the deposition of cadmium. It may be noted in passing that, in spite of the almost universal use of the cyanide solution elsewhere, surprisingly little is generally known of the electro-chemistry of the process. Soderberg's collection of data relating to the anode and cathode processes and to the chemistry of the solution is thus a valuable contribution.

The need for a larger output, more accurate control and standardised results has led to the mechanisation of the electro-plating process in the bigger plants in all countries. In America and Great Britain, fully automatic plants tend to be used, and give a standardised type of coating, whose thickness and properties are not easily changed, on a restricted range of articles. The plating industries of France and Germany appear to favour semi-automatic plants which can be more readily adapted to suit varying requirements.

One of the most important differences in practice in the various countries appeared to be the control of coatings by specification. America has taken the lead in the application of specifications which afford a control of quality, chiefly by demanding a minimum thickness of coating. It is interesting to note, however, that the lead in evolving rapid chemical methods of testing the local thickness of deposits has come from Great Britain, where the principle of using a rapid succession of drops, or an intermittent jet, of corroding liquid was first developed by Clarke for testing a number of coatings, including nickel, cadmium, and zinc. An earlier test for nickel coatings, developed by Millot in France, in which successive drops of nitro-sulphuric acid are allowed to remain in contact with the surface for one minute each, has been used for some years as a basis for the specifications of the French Railways. Although the validity of this test has not yet received published confirmation, Ballay claimed to have established standardised conditions under which it is capable of discriminating satisfactorily between good and bad quality plating.

It is important to note that it is usually the minimum and not the average thickness which is the significant criterion of the degree of protection to be expected. The tendency for unequal distribution of deposit over the surface of an article was once again illustrated by Mesle's diagrams of current distribution on silver-plated articles. Too much emphasis cannot be placed on this inherent drawback of the plating process, which has only become generally realised since the development of convenient methods of local thickness measurement. It indicates the necessity for further studies of throwing power in which the distribution of thickness is related to conditions of deposition. The modern tendency towards a reduction of plating time by increase of current density should be carefully examined in relation to protective quality, since high current density would be expected to aggravate unequal distribution of deposit.

Bright nickel-plating processes are being used to a considerable extent in America, where the high cost of labour favours processes which reduce the amount of handling and skilled finishing ordinarily necessary. Bright nickel-plating must still, however, be regarded as largely in the development stage. Little information is available on the technical advantages and disadvantages of the various processes, and, whilst advantages are to be expected in the elimination of failures in service due to removal of the coating from edges and projections during polishing, other factors are involved whose significance can only be determined by experience and research.

The restriction in the use of metallic nickel in Germany for electro-plating processes is presenting a curious problem, many platers being forced to use insoluble anodes or to manufacture nickel anodes from nickel salts by electro-deposition. The restrictions in the use of metals are encouraging the manufacture of articles from plastic materials, and processes are being developed for applying an electro-plated finish to such materials. This procedure is said to be economically satisfactory and may not be displaced if normal supplies of metal become again available. The method of electro-plating was not revealed.

The deposition of bright zinc coatings appears to have been commercially applied in America, where the Tainton process of depositing zinc on wire at very high current densities (of the order of 1000 amperes per square foot) is also used, and is said to be being developed for zinc-plating steel strip. Processes for electro-tinning steel strip as an alternative to the usual hot-dipping method are also in course of development in America ; the electro-deposition process has already been applied in Germany for the tinning of steel sheets.

A notable advance in plant is the copper-oxide rectifier, which is being used to a considerable extent in Great Britain as an alternative to the motor generator for the supply of direct current for electro-deposition.

The production of considerable quantities of the white precious metals as a by-product in the treatment of nickel ores has stimulated research into the possibility of their use as decorative and protective coatings, and commercial methods for the deposition of rhodium, platinum, and palladium have been developed. Owing to its superior reflectivity, colour, and nobility, compared with platinum and palladium, combined with its high hardness, rhodium plating has been applied on a much larger scale than that of either of the other two metals. In addition to its use as a non-tarnishing finish on jewellery and silverware, rhodium has found a very important application on reflectors of all descriptions. There is, however, a certain market, which may extend with changes in relative prices,

for platinum plating for special purposes in the chemical and metallurgical industries, and the three papers dealing with this subject, especially Atkinson's excellent historical and general review, provide a useful record of plating methods and of the properties of platinum and other precious metal coatings.

STRUCTURE AND PROPERTIES.

Papers dealing with the structure and properties of electro-deposited metals brought out a number of points of special interest. Jacquet showed that his method of anodic polishing* (preferably termed "anodic smoothing") enabled appreciably higher and more regular values to be obtained for the reflectivity of light from copper surfaces. It was suggested in the discussion that this result may indicate contamination of the surface layer with an impurity, possibly oxide, during mechanical polishing.

With the accumulation of data on the structure of electro-deposited metals, further knowledge of the mechanism by which an ordered space lattice is built up from discharged hydrated ions is urgently required. Important contributions to the solution of this problem have been made at various times, notably in recent years by the work of Erdy-Gruz and Volmer. Jacquet provided valuable data in this connection in his second paper describing the distribution of copper, determined by microscopical examination, during the early stages of deposition on crystalline copper surfaces; the anodic smoothing process was found to provide an improved technique. Copper deposited on some grains in preference to others when the current density was low and, moreover, did not grow uniformly on a single grain, but formed well-defined patterns which were probably related to the orientation of the grain. The results are in line with, and extend, Volmer's conception of "active centres."

An interesting collection of abnormalities in the microstructures of electro-deposited metals, chiefly of nickel, was provided by Cymboliste. The marked orientation caused by geometric irregularities in the surface and the banded structures suggesting periodicity during deposition (possibly allied to the phenomenon of Liesegang rings) were of special interest. It is, however, doubtful whether the general interpretation of the microstructures produced, which was made by the author in terms of the inclusion of hydroxides in the deposit, could be extended in any detail without taking many factors into account other than those referred to in the paper.

The problem of the degree to which a growing crystal of a given electro-deposited metal may be disturbed by the introduction of atoms of another metal of different atomic diameter, crystal form or lattice spacing is one of importance not only in the deposition of alloys, but also in throwing light on the structure at the interface between a deposit and a metallic base and on the effect of co-deposited impurities. The results of Phillips and Meyer's attempt to study this problem by examining the effect of additions of lead to a copper cyanide solution on the microstructure of the deposits obtained were not convincing however. The copper deposits free from lead were of very small grain size, and the conclusions drawn were not well demonstrated in the microstructures shown. The fact that complex solutions must usually be chosen for alloy deposition implies, *ipso facto*, the probability of interference with grain growth by non-metallic matter, and it is difficult to attribute with certainty the effect of additions of a second metal to the deposition of the metal only.

Theoretical conceptions of the mechanism of deposition from complex solutions—for example, silver cyanide solutions—have been changed by work such as that of Glasstone, who showed the existence of complex cations which could dissociate to give simple cations. This line of thought was further elaborated by Glazunov and Schlotter's paper, in which it was suggested, without experimental support, that the complex cation decomposes on discharge to form metal atoms which crystallise according to known laws. The fine structure of deposits normally obtained from solutions of this type still, however, remains without adequate explanation by this hypothesis.

The work upon which modern theories of the structure of electro-deposited metals have been built has been carried out with the aid of the microscope (supplemented by physical tests), electrochemical measurements, and X-ray and electron diffraction studies; hitherto, little advantage has been taken of the advances made in optical technique. The development of bright plating processes, both for base and for noble metals, has, however, encouraged the application of optical methods for evaluating "brightness," which may be defined as the ratio of true specular to diffuse reflection, independent of colour or total reflectivity; this property is readily perceived by the eye, but is difficult to evaluate quantitatively. Egeberg and Promisel described an ingenious method based on the relative values of reflectivity at various angles of incidence. Further developments along these lines should be of considerable interest, as there is no doubt that, as was indicated in the discussion and shown by Jacquet's measurements of the reflectivity of anodically smoothed copper, the factors determining the reflectivity of metallic surfaces are not completely understood.

The presence of an oxide film on corrosion-resistant metals, such as nickel and chromium and their alloys has for a long time rendered difficult the electro-deposition of strongly adherent coatings using ordinary methods of cleaning. In two papers dealing with the adhesion of electro-deposits on nickel and on chromium or chromium alloys, similar methods of dispersing the oxide film were described. Hothersall indicated a simple and effective test for detecting the presence of an oxide film on nickel surfaces which may have useful applications. Deposits formed on clean, film-free nickel exhibited different degrees of adhesion depending on the mechanical treatments previously applied to the surface. This method of investigation appears to be capable of providing useful information on the effect of mechanical treatments such as grinding and machining, &c., on the mechanical properties of the surface layers of a metal. The methods described for obtaining highly adherent deposits on nickel surfaces will be found useful, both in the engineering applications of nickel deposits and also in general nickel-plating practice. Gardam's method of removing the oxide film from chromium surfaces and simultaneously depositing a thin layer of nickel which prevents its reformation was used to study the adhesion of chromium deposits to various basis metals. No previous record of the adhesion of electro-deposited chromium has been made, partly owing to the difficulty of reinforcing

* See THE METALLURGIST, 1935–36, 10, 150.

the coating in such a way as to enable a satisfactory adhesion test to be applied. It is interesting to note that, even when no special precautions were taken to ensure cleanliness of the surface, good adhesion was obtained. Gardam's method, incidentally, provides a rapid means of enabling chromium alloys (stainless steel, for example) to be soft soldered by means of ordinary fluxes.

This brief survey of the Conference proceedings has necessarily omitted reference to a number of papers, but an attempt has been made to include the more important material of general interest. The Electro-depositors' Technical Society is to be congratulated on a successful pioneer venture which will add an important volume to the records of the Society's proceedings.

Steel for Pressure Vessels in Hydrogenation Plant.

THE increasing importance of hydrogenation processes applied to solid and liquid fuels, and the increasing attention being given to them in France, are discussed in a series of articles by Ch. Berthelot in the *Revue de Métallurgie*.[1] These articles refer to the enormous increase in the production of hydrogenation products in which France is said to have lagged behind neighbouring countries. They cover a wide range of information about the processes and economic importance of the industry, but much space is devoted to metallurgical questions involved in the choice of materials for the plant. In this connection quotations are given from the papers of Barber and Taylor[2] and of King and Fraser Shaw,[3] and extensive references are made to the experience of the Billingham plant and of the Fuel Research Board, and to the English Steel Corporation's manufacturing methods. Among the metallurgical difficulties on which information is summarised is the effect of hydrogen at high pressures and temperatures. Some experiments on different steels under these conditions have been described by Léon Jacqué in a paper on "The Mechanical Properties of Steels Treated with Hot Hydrogen Under Pressure."[4] This author has previously demonstrated the decarburising and disintegrating effect of hydrogen and claimed that a condition of cold work rendered the metal more susceptible to the action of hydrogen and so accelerated the process.[5] He carried out the work now reported on tensile test pieces 2 mm. in diameter, which, when tested on a gauge length of 14·47 mm. before alteration in hydrogen, gave results which agreed with the standard test piece of the same steel.

The specimens were cleaned, weighed, and measured, and then maintained for a given time in hydrogen under a pressure of 150 kilos. per square centimetre at a temperature of 500 deg. to 550 deg. Cent. The results of the tensile tests are given in the Table. The relative deterioration in mechanical properties increases with carbon content and is less in quenched and tempered steel than in annealed steels. Microscopic and analytical examination, and even simple weighing of the specimens, revealed decarburisation in specimens of steels 1 to 5. On the contrary, steels 9, 12, and 13, which maintained their mechanical properties after treatment in hydrogen, showed no loss of weight. In addition, steels 1 to 5, in whatever condition, underwent a distinct swelling which necessitated rethreading of the head of the test piece, a delicate operation in view of the brittleness acquired. After treatment at 500 deg. Cent. the increase in the 2 mm. diameter was usually 0·02 mm. or 0·03 mm., the maximum observed being in steel 2 with 0·32 per cent. of carbon, which, after twelve hours at 500 deg., was found to have expanded 0·08 mm. The swelling was attributed to the absorption of hydrogen before decarburisation, as observed by Inglis and Andrews in prolonged tests at 200–250 deg. Cent.[6] Heating of altered test pieces *in vacuo* at 700 deg. Cent. caused a slight improvement in mechanical properties, but did not, of course, restore the loss due to decarburisation.

The author concludes that the addition of nickel to the steel does not bring with it improved resistance to hydrogen attack, but rather the reverse. In fact, the steel which appeared from his results to constitute an effective solution to the problem of material

Mechanical Properties of Steels Before and After Treatment in Hydrogen.

Steel No.	1.	1a.	2.	2a.	3.	4.	4a.	5a.	9a.	12a.	13a.
Composition, per cent.: C	0·54	0·54	0·32	0·32	0·065	0·3	0·3	0·27	0·145	0·12	0·13
Si	0·34	0·34	0·29	0·29	0·13	0·42	0·42	0·28	0·28	0·08	0·23
Mn	0·58	0·58	0·56	0·56	0·33	0·47	0·47	0·47	0·26	0·16	0·38
Ni	0·26	0·26	0·17	0·17	0·29	2·57	2·57	2·06	0·11	0·15	0·14
Cr	0·08	0·08	0·01	0·01	0·01	0·57	0·57	0·04	5·8	5·36	3·06
Mo	—	—	—	—	—	—	—	—	0·4	0·52	0·40
V	—	—	—	—	—	—	—	—	0·25	0·37	0·30
Thermal treatment, deg. Cent. (A, annealed; Q, quenched; T, tempered)	A 900	Q 850 T 650	A 900	Q 850 T 650	A 900	A 900	Q 850 T 650	Q 850 T 650	Q 900 T 650	Q 900 T 650	Q 900 T 650
Tensile strength, tons per square inch—											
Before treatment	46	53	36	44	25	50	56	45	46	42	38
After 12 hours at 500 deg.	21	—	23	40	19	26	31	—	—	—	—
,, 50 hours at 500 deg.	18	25	20	32	17	19	33	22	45	43	39
,, 50 hours at 550 deg.	21	—	19	—	18	—	—	—	41	38	36
Elongation, per cent.—											
Before treatment	25	23	26	22	40	26	21	—	19	21	24
After 12 hours at 500 deg.	4	—	—	19	21	—	1	—	—	—	—
,, 50 hours at 500 deg.	2	nil	4	Slight	14	15	nil	1	17	18	24
,, 50 hours at 550 deg.	nil	—	18	—	—	—	—	—	24	25	25

[1] September to December, 1936, Vol. 33, pages 566, 619, 677, and 727.

[2] Inst. Mech. Engineers, 1934.

[3] Chemical Eng. Congress, 1936.

[4] *Comptes Rendus*, Nov. 9th, 1936, 203, 936.

[5] *Comptes Rendus*, 1932, 195, 878.

[6] *Journ.*, Iron and Steel Inst., 1933 (2), 128, 383.

for plant for hot hydrogen under pressure, contained 3 to 6 per cent. chromium, 0·5 per cent. molybdenum, no nickel, and very little carbon. Such a steel, or one to which other additions of vanadium or tungsten are made, is already in wide commercial use for pressure vessels.

Electrodeposited Lead for the Protection of Iron and Steel.

By F. W. HAY, D.Sc.

THE electrolytic deposition of lead on iron and steel has been found to provide a suitable means of permanent protection against atmospheric influence, fumes, corrosive gases and the like. It is well known that the common practice of coating iron constructions, which are exposed to the air of industrial centres, stations, factories, &c., with so-called anti-corrosive paint offers only a limited protection against the influence of the atmosphere. The coating of paint has to be renewed from time to time, thus entailing high maintenance costs. Galvanising with zinc offers better protection, but even galvanised iron will not withstand corrosive gases, such as sulphur dioxide, which are common constituents of the air in all industrial centres.

It has been found that a much more effective and, in fact, a permanent protection of iron constructions can be obtained by coating the structural parts, such as girders, iron supports, profile irons, stays, &c., with a thin film of lead obtained by electrolytic deposition. The film of lead so obtained forms a continuous layer, which is firmly amalgamated with the surface of the iron, so that it cannot be detached, and since lead is capable of withstanding corrosive gases, fumes, &c., to an almost unlimited extent, any rusting or corrosion of the iron by fumes is effectively avoided.

Whilst it is feasible to protect certain kinds of plant, such as an iron pan, against chemical agents by so-called homogeneous lead lining, *i.e.*, by a layer of sheet lead of, say, ⅛in. in thickness, it would be much too costly to protect iron structures in this manner. Besides, many iron structures, such as window frames, would become distorted by the heat which is generated in this older process of lining with sheet lead. In many cases, moreover, the great increase in weight produced by lining with sheet lead or by dipping into molten lead would be a serious objection.

The electrolytic deposition of lead is carried out in the cold, and can be so adjusted that the coating of lead obtained varies in thickness from 0·02 mm. to 3 mm. and over, according to the degree of protection required. Any deformation of the original material or plant by heating is, of course, out of the question.

The above process of electrolytic lead plating has been the subject of prolonged investigation in Switzerland, and is now widely used in that country for preventing the rusting or corrosion of iron and steel structures. It has been found particularly useful for protecting iron used in building railway stations, tunnels, bridgework, roof construction, supports for electric lines, channel irons for cables, earth poles for taking to earth high-tension currents at power stations, as well as for a large variety of structural parts used in the erection and equipment of factories, foundries, and chemical works.

The cost of this process, though slightly higher than galvanising, is quite moderate considering that it produces permanent protection. Its field of application is almost unlimited, since it can usefully be applied whenever it is of importance to reduce the cost of maintenance to a minimum.

Lead offers, of course, infinitely better protection than paint. Contrary to layers of paint, the lead coating obtained by electrolytic deposition is so intimately welded to the parent material that no line of demarcation between the lead and the iron can be observed if a cross section of the lead-plated material is examined under the microscope. Any contractions or expansions of the iron structures due to changes of temperature are thus readily followed by the coating of lead, and no peeling off need be feared. The lead coating thus resists the influence of the atmosphere, fumes, &c., for an indefinite period.

The Alloys of Iron, Vanadium and Carbon.

IN a review of the constitution of the iron-vanadium-carbon system published six years ago, some of the differences between the results of German and Japanese researches which had at that time just been published were discussed in detail.[1] Opinions on the constitution of the iron-vanadium-carbon alloys still diverge considerably from one another,

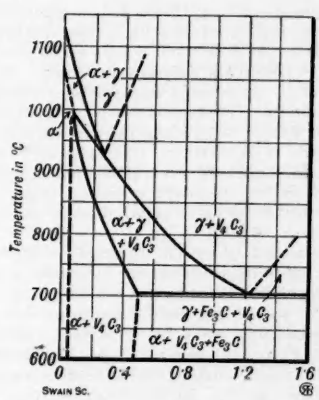


FIG. 1—*Constitution of the 2 per cent. Vanadium Steels, according to M. Oya.*

and in particular sufficient evidence is not available to enable a decision to be made between the diagrams of Vogel and Martin[2], and of Oya.[3] In a paper on "The Ternary System, Iron-Vanadium-Carbon," F. Wever, A. Rose, and H. Eggers[4] have, in the first place, presented a very full discussion of the differences between the conclusions of the German and Japanese authors, and have then described some experimental work carried out with the object of throwing light on several features under dispute.

One of the fundamental differences between the two types of diagram is that according to Vogel and Martin the vanadium-V_4C_3 system contains a γ-phase (pure vanadium austenite), which forms an unbroken series of solid solutions with γ-iron, whereas in Oya's diagram the homogeneous field disappears at a relatively small vanadium content. This makes a

considerable difference to the interpretation of the constitution of alloys of low vanadium content as is illustrated by the sectional diagrams (parallel to the iron-carbon side) for 2 per cent. vanadium steels, as shown in Figs. 1 and 2.

Wever, Rose, and Eggers prepared a series of alloys containing 0 to 1·9 per cent. of carbon with approximately 0·5, 1, 1·5, 2, and 5 per cent. of

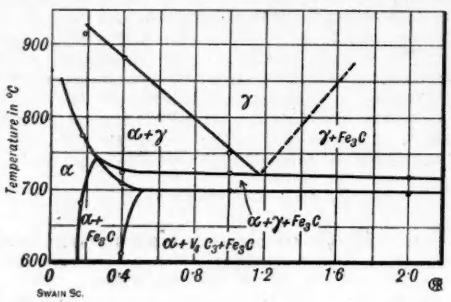


FIG. 2—*Constitution of the 2 per cent. Vanadium Steels, according to R. Vogel and E. Martin.*

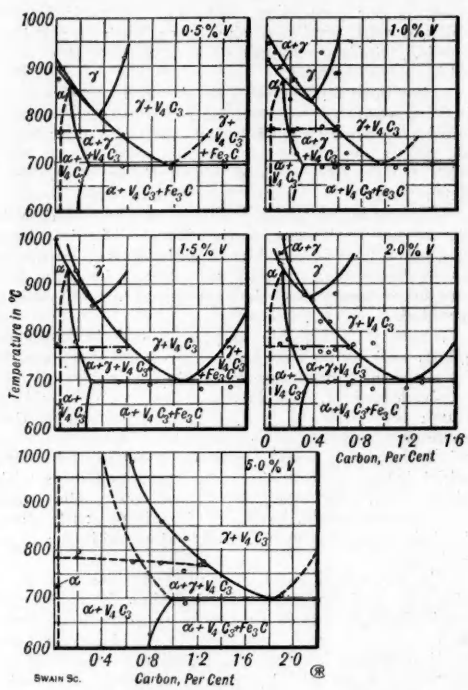
vanadium, and studied their constitution by means of thermal and microscopical methods. Their general conclusions were in support of the diagram of Oya, and are expressed in the series of sections parallel to the iron-carbon side (Figs. 3–7). They found the γ field to be restricted to a high temperature region, and the large field marked γ by Vogel and Martin to be never free from vanadium carbide. The lower point of the γ region was found to rise with increasing carbon content. That vanadium carbide is soluble in γ to an extent depending on carbon content and temperature is shown by the resistance measurements made on quenched test pieces by H. Hougardy,[5] and by the reduction in the critical cooling velocities of vanadium steels as compared with plain carbon steels.[6]

In Vogel and Martin's diagram there is region of very small temperature range below the γ eutectoid point in which the phases $\alpha+\gamma+Fe_3C$ are stable. This region with 2 per cent. vanadium, as in Fig. 2, extends to about 4 per cent. of carbon, the boundary of the $\gamma+Fe_3C$ and the $\gamma+Fe_3C+V_4C_3$ fields. At a small interval (10 deg. or 20 deg.) below the eutectoid temperature the residual γ is resolved into $\alpha+V_4C_3$, giving the main field of stability at room temperatures, $\alpha+Fe_3C+V_4C_3$, which is shown in both diagrams (Figs. 1 and 2). Wever, Rose, and Eggers found no evidence, thermal or microscopical, for the $\alpha+\gamma+Fe_3C$ field or for the consequent $\alpha+Fe_3C$ field in the 2 per cent. vanadium alloy. They hold that the $\alpha+\gamma+Fe_3C$ field does not extend to 6 per cent. vanadium, and 1·8 per cent. carbon as in Vogel and Martin's diagram, but possibly to about 0·35 per cent. vanadium and 0·93 per cent. carbon as suggested by Oya; at any rate, they found that it had disappeared before 0·5 per cent. of vanadium was reached. Precipitation of V_4C_3 from the γ solid solution was shown by differential curves in the region of 0·4 to 0·6 per cent. of vanadium at 900 deg. Cent.

In the immediate vicinity of the iron-vanadium side of the diagram a ternary α solution is stable, but no attempt was made to determine the boundary of the region between the α and the $\alpha+V_4C_3$ fields.

In view of the temper hardening which can occur in vanadium steels, the solubility of carbon in vanadium ferrite is a matter of interest.

One of the discrepancies in previous work has been the temperature of the plane of four-phase equilibrium $\alpha+\gamma+Fe_3C+V_4C_3$; in other words, the influence of vanadium on the A_1 point. Wever, Rose, and Eggers devote considerable attention to this question, and on the evidence of cooling curves taken at different rates between 15 deg. and 50 deg. per minute and extrapolated to correct for undercooling they arrived at the conclusion that it occurs at 695 deg. Cent., or 26 deg. below the A_1 point of carbon steel. They are alive to the possibility that their correction for undercooling may be inadequate and therefore carried out a direct dilatometric comparison of a vanadium steel containing 1·81 per cent. of vanadium and 1·07 per cent. of carbon with a eutectoid carbon steel. By this means the relative position of the points in the two steels can be ascertained independently of any accurate temperature measurement, and at a very slow rate of change of temperature. They were found to be almost identical. The measurements were repeated in a dilatometer



FIGS. 3–7—*Sections through the Ternary Iron-Vanadium-Carbon System at Constant Vanadium Contents (Wever, Rose and Eggers).*

recently designed by H. Lange at the Kaiser-Wilhelm Institute, Düsseldorf, and the temperatures of the A_1 points were again found to coincide within ±1 deg. Cent.

Hardness testing of quenched specimens of vanadium steels and plain carbon steels showed that in both cases hardening began between 715 deg. and 722 deg. Cent. This confirms the conclusion that the critical point is the same in plain carbon steels and

vanadium steels; but it may be noted that the actual temperature agrees with the A_1 point for carbon steels, but is some 20–27 deg. higher than the 695 deg. arrived at by the authors for vanadium steels. It appears that the corrections applied for undercooling may have been too low, and it seems to be a matter for consideration whether a more accurate value would not be obtained from heating curves which have usually shown a small rise, viz., Hougardy,[7] 10 deg.; Putz,[8] 10 deg.; Oya,[3] 15 deg.; Abram,[9] 12 deg.

However, the authors do not pursue the matter further, but content themselves by stating that the four-phase plane must lie in the immediate vicinity of the temperature of the iron-carbon austenite → pearlite transformation, and that for practical purposes it is therefore idle to speculate on the eutectoid or peritectoid nature of the four-phase reaction.

The iron-vanadium-carbon system presents difficulty in investigation on account of the occurrence of the difficultly soluble V_4C_3 in the alloys, permitting superheating in the heating curves and making the attainment of equilibrium conditions, by annealing, uncertain. When a homogeneous ternary phase has been secured the undercooling which occurs in taking cooling curves makes it almost impossible to get accurate measurements of the transition temperatures. These features of the iron-vanadium-carbon system complicate the interpretation of the experimental results and are largely responsible for the differences of opinion which have arisen with regard to the constitution of these alloys. The paper of Wever, Rose, and Eggers is a welcome attempt to reconcile some of these differences and to provide new experimental data of value in deciding between the contrary views of previous authors.

[1] THE METALLURGIST, 1931, 7, 91, 98, and 115.
[2] *Archiv Eisenhüttenwesen*, 1930–31, 4, 487.
[3] Science Reports, Töhoku Imp. Univ., 1930, 19, 331.
[4] *Mitt. K.W. Inst. Eisenforschung*, 1936, 18, 239.
[5] "Die Vanadinstähle," 1934, Verlag Gärtner, Berlin.
[6] H. Esser and E. Majert, *Archiv Eisenhüttenwesen*, 1933–34, 7, 319.
[7] *Archiv Eisenhüttenwesen*, 1930–31, 4, 497.
[8] *Metallurgie*, 1906, 3, 635.
[9] *Journ. Iron and Steel Inst.*, 1934, (2), 130, 351.

Iron Oxide Films.

By H. A. MILEY, M.A., M.S., Ph.D.,
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No. I.

A NEW electrical method for measuring the thickness of oxide films has been described and the values given for the films formed on iron when exposed to air at several temperatures.[1] The method requires that the time be observed for the cathodic reduction of a film by a constant electric current, and from the millicoulombs thus obtained the thickness is calculated by means of one of Faraday's Laws. The electrolyte used is M/5 ammonium chloride solution, and it has the advantage that (*a*) when tinted specimens are kept in it for times long as compared with those of reduction experiments, there is no alteration of colours nor any appreciable loss of thickness (when acid is used as the electrolyte, the films are rapidly reduced as noted by colour changes or electrical measurements, and are soon destroyed completely through the local cells—ferric oxide/acid/iron—formed in the cracks or pores of the oxide), and (*b*) it introduces no complications at the anode through polarisation changes.

A similar method[2] was used to measure the thickness of silver iodide films, and the results agreed with those of two other methods (iodometric and gravimetric).

THICKNESS OF THE FILMS.

(1) *Electrical Method.*—The electrical method has given numbers (Table I) for the tinted oxide films,

TABLE I.—*Thickness (Mean General Intercepts) of Iron Oxide Films in Ångström Units* (1 Å = 10^{-8} cm. = 0·1 μ).

Iron tinted to	Electrical (New)	Optical (Constable)	Gravimetric* (New)
	Å.	Å.	Å.
Straw	440	460	390
Reddish-yellow...	530	520	470
Red-brown ...	560	580	500
Purple	625	630	560
Violet	695	680	625
Blue	725	720	650

produced by heating iron in air at 350 deg. Cent., which agree satisfactorily with the results of three other methods of measuring the film thickness (optical, chemical, and gravimetric when corrections are made for the invisible oxide formed on the specimens before the first weighing). The apparent disagreement in the past between the optical and gravimetric results has been explained as being due to this invisible oxide. The differences in the results of the several methods have been explained by the fact that they do not measure the same things.

(2) *Optical Method.*—Constable[3] has measured the thickness of these films optically from the spectrophotometric value of the wave-length of light of maximum or minimum reflection and the index of refraction of the oxide. The good agreement with his value is significant, as will be seen later, since his measurements (*a*) are independent of the composition of the oxide (being dependent on the mean distance between the inner and outer reflecting surfaces of the oxide layer), and (*b*) do not include the embedded oxide.

(3) *Chemical Method.*—Evans and Stockdale[4] have removed films from iron by electrolysis in an atmosphere of hydrogen, and measured their thicknesses chemically from determinations of the amount of iron which they contained. Their results indicated that beneath the *homogeneous film* of oxide was a *mixed zone* of oxide and metal. They succeeded in stripping the homogeneous films of intermediate thickness (those in and near the region of the first-order straw-yellow) and obtained a thickness value agreeing well with Constable's value for the same film; in this case the edges of the specimen were painted so that the anodic attack had to proceed through the film. When the edges were not painted, the attack was made principally from the edges and the straw-yellow films were undermined below the mixed zone and yielded a *total oxide* value which was approximately twice the amount provided by the homogeneous film alone. For the less perfect films (the thick ones containing cracks and the thin ones with pores) the values obtained appear to represent, in most cases, only the total oxide. The volume of the oxide is greater than the metal it replaces, and this gives rise to compressional energy in the oxide which

* Corrected for the invisible film on the surface at the time of the first weighing, but not for any oxide of the mixed zone that might have been incorporated in the homogeneous film during heat tinting.

is small in the thin films, and increases as the films thicken; it reaches a maximum value for iron in or near the region of the straw-yellow films, beyond which the energy becomes small again through the cracking of the oxide films. The stresses are possibly great enough only in the films of intermediate thicknesses to effect a separation along the boundary of the homogeneous film and mixed zone, with the aid of the electrolysis.

The electrical results show several agreements with these film-stripping and chemical-estimation results:

(*a*) Two end points are observed, one for the completion of the reduction of the oxide in the homogeneous film and the other for the moment when the reduction of the accessible oxide in the mixed zone gives place to the evolution of hydrogen.

(*b*) The first end point is more pronounced than the second one, as might be expected from Evans and Stockdale's description of the oxide zones.

(*c*) The first end point leads to a value for the thickness of the homogeneous film of the straw-yellow region, which is in good agreement[5] with Evans and Stockdale's value, and also with Constable's value for the same film, 440, 420, and 460 respectively.

(*d*) The second end point represents a total oxide value which is nearly twice the amount of the oxide in the straw homogeneous film.[6]

(*e*) If the amount of oxide of the homogeneous film (as determined, say, by the electrical method) for the straw-yellow and mauve films be subtracted respectively from the total oxide values obtained chemically and electrically for these films, it is found that both show a decrease in the embedded oxide value as the homogeneous film thickens. This is in agreement with the idea that the mixed zone is a near-the-surface effect, resulting from abrasion or other surface treatments, and with Evans and Stockdale's conclusion that the boundaries of the mixed zone come closer together as the film thickens.

(*f*) The differences observed in their film-stripping results for the thin, intermediate, and thick first-order films may be recalled in studying the curves given for these films.[1] Some differences in these three films have been explained as due to pores in the thin ones and cracks in the thick ones. Other effects of these discontinuities in the films have been reported elsewhere.[7]

(4) *Gravimetric Method.*—Vernon[8] measured the thickness of the first-order orange film on iron from the weight increment produced from heat tinting and the density of the oxide, and obtained a thickness value of 56 Å, or 140 Å when his value is brought to the same definition of "thickness" as that[9] used in the above comparisons. With a fixed method of abrasion and time of exposure to pure air the weight increment on tinting the specimens to straw colour gave a mean value of 180 Å, which is of the same order of magnitude as the value Vernon gave for the orange film. When specimens were identically treated and measured electrically instead of heat tinting, they were found to carry a mean thickness of 210 Å for the homogeneous film value. By adding these values, 390 Å is obtained for the homogeneous straw film. This is 50 Å less than the value obtained in the present work for this film. Now it may be considered that this 50 Å is the amount of the embedded oxide which is incorporated in the homogeneous film as it thickens on heat tinting.[10] Thus it appears that a tinted film formed on an abraded surface contains (*a*) the homogeneous part of the invisible oxide carried by the specimen at the time of the first weighing, (*b*) much of the oxide resulting from the oxygen uptake on tinting, and (*c*) some oxide incorporated from the mixed zone on thickening during heat tinting.

(5) *Simple Colour Method.*—By assuming that the colour of the film is dependent entirely upon the wave-length of the light of maximum absorption, an estimate of the thickness of a given film may be obtained by dividing the thickness of the air film required for minimum transmission of the same wave-length by the index of refraction of the oxide for this wave-length. This assumption has been considered to be permissible for oxide films on copper,[11] and it might be of interest to obtain some values for iron oxide films about the region of the straw-yellow by this method. From Rollett's values[12] of 1000, 1070, and 1160 Å for the respective thicknesses of the air films needed to give the colours brownish white, clear brown, and dark brown by transmitted light, and Kundt's value[13] of 2·36 for the index of refraction of iron oxide for blue light, the values 424, 453, and 492 Å are obtained for the oxide films which are nearest to these respective colours. The first two colours possibly represent more nearly what has been considered to be the films of the straw-yellow region; the agreement is, in any case, surprisingly close to the values given by the other methods for the films of this region.

Thus it appears that the optical, chemical, electrical, and gravimetric methods (when the gravimetric is corrected for the oxide carried at the time of the first weighing) have been shown to be in satisfactory agreement in their measurements of the thickness of the straw-yellow homogeneous film and that the equivalent-air-thickness/index-of-refraction method gives values for the region of this film which are of the right order of magnitude.

GROWTH OF THE FILMS.

The small weight increments and the shape of the oxidation/time curves obtained gravimetrically by Vernon[8] (*loc. cit.* p. 1676) led him to believe that it requires days to develop a very thin oxide film on the surface of abraded iron exposed to dry air at ordinary temperatures. References have been given,[1, 14] to considerable optical data, electro-chemical evidence, electron diffraction measurements, and the present electrical measurements which point to a rapid rate of oxidation for most common metals when first exposed to dry air, and particularly for iron which is believed to form an oxide film, during the first few seconds or minutes, which is sufficiently protective to cause the rate of oxidation to become relatively slow on further exposure to dry air at ordinary temperatures. There are at least three factors which greatly influence the amount of oxide produced before the film becomes sufficiently protective to render the rate of oxidation slow:

(*a*) Relatively high transitory temperatures, such as might be expected from abrasion, polishing, turning, or other treatments where "sliding metal" effects[15] are incurred, can greatly influence the amount of oxide formed.

(*b*) The accessible area of the metal is very important, and may be several times the apparent area[16] (that obtained by multiplying the width by the length). In addition to these two areas for an abraded surface, there is the contour area which follows the contour of the surface, and may be said to separate the inside from the outside of the metal. The accessible area includes the areas in the cracks and the parts of the contour area that are between the cracks. The apparent discrepancies resulting from

the different meanings that have been assigned to the term "area" of a metal surface will be discussed elsewhere. The differences in the published results that have been caused by the fact that all authors have not adopted the same definition for the term "thickness," when applied to an oxide film on a metal surface, have already been discussed.[1] The mean general intercept is perpendicular to the plane of the apparent area, whilst the mean local intercept is perpendicular to that of the contour area. All the surface irregularities and the Beilby amorphous layer of a polished metal, and the corrugations, mixed zone fissures, and the "shattered metal" of an abraded metal[4] will greatly influence the accessible area, and hence the uptake of oxygen before the rate of oxidation becomes slow.

(*c*) The film may be repeatedly cracked while the stresses, caused by abrasion or other treatment, are being relieved, thereby keeping fresh metal exposed to oxygen and increasing the amount of oxidation. A very smooth surface of unstrained metal[14] (such as an iron "mirror" surface produced by evaporation and condensation of the metal *in vacuo*) may acquire a film thickness of only 10 to 30 Å, whilst a coarsely abraded iron surface must acquire an amount of oxide equivalent to a relatively thick film (if it were spread uniformly over the apparent area) before the rate of oxidation will become slow. The slow oxidation rate observed by Vernon and the shape of his oxidation/time curves, which he considers important, do not necessarily appear inconsistent with these views.

Hunter[17], in studies of the photo-electric threshold shifts for turned surfaces of several metals, obtained results which caused him to postulate an oxygen film adsorbed on the surfaces of the metals during the time of the experiments (two minutes) rather than an oxide film. Rentschler and Henry,[18] on the other hand, in their studies of the effect of oxygen upon the photo-electric thresholds of metals, found that when even a small amount of oxygen was permitted to react with the surface of the metal (produced by evaporation and condensation *in vacuo*) that the threshold shifts were in the expected direction to indicate the formation of protective oxide films. As suggested by Hoar,[14] these apparently conflicting results are both in agreement with the view which has been expressed concerning the oxidation of strained and unstrained metals; the expected restraint on the photo-electron transmission was not realised in Hunter's experiments possibly because the film was repeatedly cracked during the time of the experiments, through the relief of the stresses resulting from the turning operation.

Dobinski[19] has reported a rapid oxidation of metals, including iron, when polished in air. His electron diffraction patterns of the metals polished in benzene or pentane did not show the rings and bands characteristic of an oxide at first, but gradually acquired these oxide evidences on exposure to air.[20] When he polished or burnished the specimens in air, as previous electron diffraction experimenters had done, the oxidation always appeared to be complete, as far as could be judged from the oxide layers participating in the electron diffraction effects recorded in the patterns. It is not surprising that this method would fail to follow a further slow oxidation, such as can be measured gravimetrically. Dobinski concluded that metal surfaces polished in air are always "heavily" oxidised, and that the amount of the oxidation is enhanced when different oxides in the presence of water are employed as the polishing media. He further states that the oxide layer produced when the surface is polished in air is much greater than the protective layer obtained by exposing an unoxidised surface (one polished in benzene or pentane) to air.

Nelson[21] found that iron (which had been evaporated and condensed *in vacuo*) gave electron diffraction reflection patterns characteristic only of α iron before exposure to air, but after exposure to dry air at room temperature and atmospheric pressure for a brief period, the patterns were "markedly" different and in good agreement with what might be expected for a thin film of oxide on the surface. The time of the rapid oxidation was less than 4 min., for little change could be detected in the patterns by continuing the exposures at room temperature after this period, but heating the specimens for only 3 min. to 7 min. at 150 deg. to 200 deg. Cent. caused the iron rings to disappear and the oxide ones to become much stronger.

A comparative study of Dobinski and Nelson's results shows that they indicate a rapid oxidation followed by a relatively slow rate. As might be expected from the oxidation of smooth and unstrained metal, Nelson's results point to a film, which is still quite thin, before the rate becomes slow, whilst Dobinski's results, with rougher metal surfaces and strained metal, indicate that the oxidation is much more severe before the film becomes highly protective.

References.

[1] U. R. Evans and H. A. Miley, *Nature*, 1937, 139, 283; H. A. Miley, Iron and Steel Inst. Carnegie Scholarship Memoirs, 1936, 25, 197. The reader will find in these papers more references and a discussion of a number of the questions mentioned in the present paper; others will be discussed elsewhere.

[2] U. R. Evans and L. C. Bannister, "Proc.," Roy. Soc. (A), 1929, 125, 370, 380.

[3] F. H. Constable, "Proc.," Roy. Soc. (A), 1928, 117, 376, 386.

[4] U. R. Evans and J. Stockdale, *J.* Chem. Soc., 1929, p. 2651.

[5] In comparing the different values for the straw-yellow films it should be remembered that the intensity/wave-length absorption band is much broader for these films than it is in the regions of most of the interference colours, and that it is accordingly more difficult to obtain fixed values for this film, by any method, than for the films of most other colours.

[6] As the oxide is reduced from the fissures of the mixed zone, the increasing electrolytic resistance may raise the potential of the cell to the value required for the evolution of hydrogen before all the relatively inaccessible oxide has been reduced; if so, the electrical value may represent only approximately the amount of the oxide in the mixed zone.

[7] U. R. Evans, *Nature*, 1926, 118, 51.

[8] W. H. J. Vernon, "Trans.," Faraday Soc., 1935, 31, 1674.

[9] "Thickness" is here considered to be the mean intercept made by normals to the general plane of the surface, whilst some have defined it as the mean of the intercepts made by the film on the lines drawn perpendicular to the local plane of the surface.

[10] The same value would be provided for the homogeneous film by considering that the amount of oxide incorporated from the mixed zone was, say, x Å more than the 50 Å provided that x amount of the 180 Å was considered to have been formed in the mixed zone beneath the straw homogeneous film. It is reasonable to suppose that x is not zero.

[11] J. S. Dunn, "Proc.," Roy. Soc. (A), 1926, 111, 214; F. H. Constable, "Proc.," Roy. Soc. (A), 1927, 115, 581; 1929, 125, 633.

[12] A. Rollett, *Sitzungsber. Akad. Wien*, 1878, 77, 229.

[13] A. Kundt, *Ann. Physik*, 1888, 34, 484.

[14] T. P. Hoar, *Met. Ind.*, 1936, 49, 177.

[15] F. P. Bowden and K. E. W. Ridler, "Proc.," Roy. Soc. (A), 1936, 154, 640.

[16] F. P. Bowden and E. K. Rideal, "Proc.," Roy. Soc. (A), 1928, 120, 59, 80,

[17] J. S. Hunter, "Proc.," Roy. Soc. Edin., 1934, 54, 102; *Phil. Mag.*, 1935, 19, 958.

[18] H. C. Rentschler and D. E. Henry, *J.* Opt. Soc. Amer., 1936, 26, 30.

[19] S. Dobinski, *Nature*, 1936, 138, 31; *Phil. Mag.*, 1937, 23, 397.

[20] The specimens were not exposed to air before the first

patterns were made enough for an appreciable amount of oxide to be formed; they were placed in the camera, while still wet with the benzene or pentane, and the vacuum was developed immediately.

[21] H. R. Nelson, *Nature*, 1937, 139, 30; Private Communication, 1937, March 19th; *J. Chem. Phys.*, 1937, 5, 252.

In these last two references he has stated that his results do not distinguish between Fe_3O_4 and γ-Fe_2O_3.

(To be continued.)

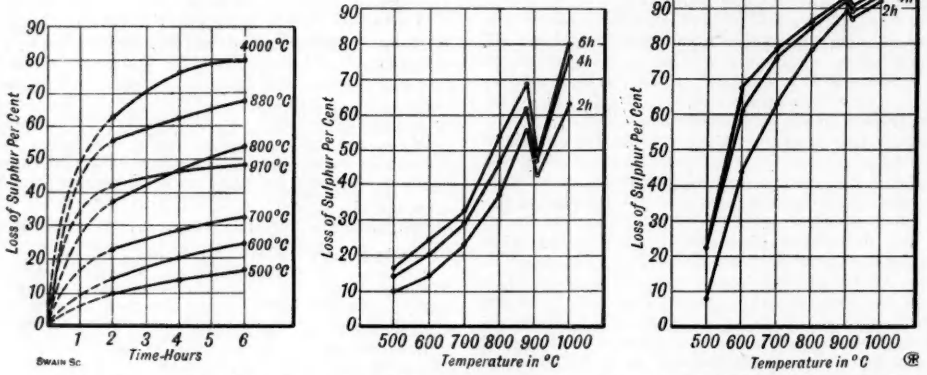
Desulphurisation by Hydrogen.

HEATING in hydrogen has not only a decarburising effect on solid steel, but also produces desulphurisation. The mechanism of this desulphurisation and the effect of composition and of temperature on the rate of the reaction have been described in a paper by W. Baukloh,* on "The Desulphurisation of Iron by Hydrogen."

Dealing first with the relative stability of different sulphides when heated in hydrogen, he found that, like calcium sulphide (CaS), manganese sulphide (MnS) did not decompose when heated in hydrogen at 1000 deg. Cent. Iron sulphide (FeS), on the other hand, was already attacked at 400–450 deg. Cent., and at 1000 deg. Cent. there was a rapid, though not complete decomposition, since after the first surface desulphurisation, the sulphide was protected from further attack by the outer layers of iron formed on the particles. Thus, for example, at 1000 deg. Cent., 38 per cent. of the sulphur was lost in 15 minutes, but after three hours the loss had not increased to more than 42 per cent.

The iron-sulphur alloys studied by Baukloh contained about 0·4 and 0·9 per cent. of sulphur, and were made from electrolytic iron, and a sulphur-rich iron alloy, manganese being introduced when necessary by the addition of 92 per cent. ferro-manganese. The desulphurising experiments were made on turnings about 1 mm. thick heated in a current of dry hydrogen, passed through at a rate which was a little higher than that shown by experiment to be necessary to give the maximum desulphurising effect at a given temperature.

The percentage desulphurisation was determined for different times of exposure to hydrogen at different temperatures and plotted in a series of curves. An interesting feature of these was the sudden fall in the desulphurising action of hydrogen at about 900 deg. Cent. The curves representing the progress of desulphurisation at 800 deg. and at 880 deg. Cent. both fell above that expressing the rate at 910 deg. Cent. (Fig. 1). It is clear therefore that at about 900 deg. Cent. there is a discontinuity in the progress of the reaction in relation to temperature (Fig. 2). Baukloh was able to link up this discontinuity with two examples of a similar effect observed by him previously. Baukloh and Kayser† found that the diffusion of hydrogen in iron was retarded by the change from body-centred α iron to the denser face-centred lattice of γ iron. With further rise in temperature the rate of diffusion increased again to a higher figure, but the effect of the $\alpha \rightarrow \gamma$ change was to introduce a check in the rise in rates of diffusion. The influence of these diffusion rates on the course of a reaction can be followed in Baukloh and Guthmann's‡ work on the decarburisation of steel. The discontinuity in the rate of diffusion at the $\alpha \rightarrow \gamma$ change is clearly shown in the check experienced in the rise in rate of decarburisation in the same temperature region. In the light of these results it is possible to interpret the character of the desulphurisation curves. The desulphurising process consists of two stages, the first being the diffusion of hydrogen into the metal and the second the true reaction of the sulphide with hydrogen. That which determines the final rate of desulphurisation is the slower of the two, viz., the diffusion of hydrogen. Hence the discontinuity observed in the rate of diffusion at the A_3 point is revealed in the desulphurisation process as it is also in decarburisation. A further confirmation of this explanation is found in the results of experiments on the desulphurising of steels containing manganese. In these the discontinuity in the rate of desulphurisation in relation to temperature was displaced to an extent exactly corresponding with the alteration of the temperature of the A_1 point brought about by the addition of the manganese (Figs. 3 to 5). Microscopic examination showed no edge effect, and the desulphurisation had



FIGS. 1 AND 2—*Desulphurising of Iron with 0·40 per cent., Sulphur and 0·09 per cent., Manganese by means of Hydrogen.*

FIG. 3—*Desulphurising of Iron with Sulphur 0·83, Manganese 0·11 per cent.*

* *Metallwirtschaft*, 1936, 15, 1193.

† *Zeit. Metallkunde*, 1935, 27, 281.

‡ *Zeit. Metallkunde*, 1936, 28, 34 THE METALLURGIST, 1936, 10, 146.

the appearance of having taken place over the whole specimen equally.

A further effect of increasing the manganese content was to reduce the amount of desulphurisation. Thus, while the desulphurisation of an alloy with 0·83 per cent. sulphur and 0·11 per cent. manganese was 96 per cent. after six hours heating in hydrogen at 1000 deg. Cent., in an alloy with equal sulphur content and manangese 0·97 per cent. treated under identical experimental conditions, the desulphurisation was 60 per cent., and with manganese 1·25 per cent. it

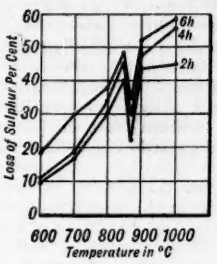


FIG. 4—*Desulphurising of Iron with Sulphur 0·83, Manganese 0·97 per cent.*

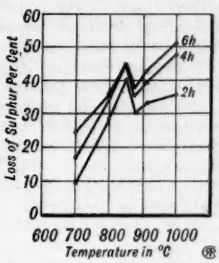


FIG. 5—*Desulphurising of Iron with Sulphur 0·83, Manganese 1·25 per cent.*

was only about 50 per cent. This was due to the stability of MnS under hydrogen treatment. Desulphurisation diminished with increasing manganese content, until, with a ratio of manganese to sulphur corresponding to that required theoretically for the formation of MnS, hydrogen had no desulphurising action at temperatures up to 1000 deg. Cent. (With 0·83 per cent. of sulphur manganese in accordance with this ratio would be 1·43 per cent.)

From this it appears that steels of normal manganese and sulphur contents are unlikely to be desulphurised by hydrogen, but the exact compositions of the alloys on which Baukloh's statement was based are not given, and the conclusion should perhaps be accepted with the reservation that with the small amount of sulphur present in steel rather more than the equivalent amount of manganese would be required to convert it wholly into MnS and so completely inhibit desulphurisation.

Precipitation-Hardening of Alloys of Beryllium with Copper and Nickel.

DURING recent years a great deal of research has been directed towards the elucidation of the mechanism of precipitation hardening in alloys. In this connection two interesting papers have been published by H. Bumm* and H. Lay† dealing with the decomposition of supersaturated solid solutions of beryllium in copper and nickel respectively.

The copper alloys contained 2·2 to 2·5 per cent. beryllium and were homogenised *in vacuo* at 800 deg. Cent. before quenching. The progress of precipitation was followed by micrographic examination after etching with ammonia or ferric chloride solution and also by X-ray measurements of the lattice constants.

Heating of the quenched alloys after cold working resulted in a more rapid precipitation of CuBe in all cases. At 350 deg. Cent. precipitation starts along the grain boundaries and progresses inwards to an extent which is greater in cold-worked than in unworked alloys. When the specimen is etched with ferric chloride solution the areas in which precipitation has taken place are blackened; the progress of precipitation can thus be followed by measuring the black areas. In worked alloys heated at 350 deg. Cent. growth of these areas ceases in 10 min. and in cast alloys in 22 min. In neither case do the areas cover the entire surface of any of the crystallites, and the maximum size of the areas is twice as great at 350 deg. as at 250 deg. Cent. At 500 deg. Cent., on the other hand, the whole surface of the specimen blackens on etching after heating for only 7 min. Very prolonged heating at the lower temperatures, however, results in microscopically invisible precipitation in the light-coloured areas, and eventually, after 100 hours, in an inversion in the distribution of the areas, the original light areas becoming dark and the dark areas light coloured. At a magnification of 1000 diameters the latter areas show streaks of the precipitated phase, indicating that the originally disperse particles have coagulated.

X-ray measurements of the lattice constants during precipitation show that at 250 deg. and 350 deg. Cent. there is a period of induction before any lattice change occurs. This period is shorter the higher the temperature, and the greater the cold work to which the alloy has been subjected. At 350 deg. Cent. the change in lattice constants sets in rapidly at the end of the period of induction, whereas at 250 deg. it is much more gradual.

The above results are considered to show that precipitation takes place in two ways:—In the dark zones the new phase separates along lattice planes parallel to the grain boundaries and the precipitation is autocatalytically accelerated, whereas in the light areas it occurs throughout the body of the lattice in a microscopically homogeneous manner. Both types of precipitation occur simultaneously, but the latter type has a period of induction and with increasing temperature gives place more and more to the former type until at 500 deg. Cent. this entirely controls the reaction. These results are similar to those obtained by Bumm and Dehlinger‡ on silver-copper alloys.

When a nickel alloy containing 1·9 per cent. beryllium is quenched from 1100 deg. Cent. and then reheated at 350 deg. Cent., the Brinell hardness increases from 150 to 250 in 7 hours, then decreases by about 10 units during the next 3 hours, after which it increases linearly, reaching 350 in 70 hours; the lattice constants remain unchanged until the tenth hour, after which the proportion of precipitated NiBe increases rapidly. This behaviour is characteristic of microscopically homogeneous precipitation. The original sharp increase in hardness is attributed to a preliminary process of complex formation similar to that which occurs in the cold ageing of duralumin.

When the quenched alloy is reheated at 500 deg. Cent. the hardness rises rapidly, reaching 500 in 30 min., and then rising more slowly to 600 in 30 hours. The lattice constants also rise, after a very short period of induction, to a maximum in 2·5 hours, and then decrease to a constant value in 10 hours.

* *Z. Metallkunde*, 1937, 29, 30.
† *Ibid.*, 32.

‡ *Metallwirtschaft*, 1936, 15. 89; THE METALLURGIST, 1935–36, 10, 134.

The etched micro-section shows black areas round the grain boundaries after 30 min., and these extend over about half the surface in 20 hours. Their hardness is appreciably lower than that of the bright areas, the difference amounting to 100 units after 30 hours. Thus the microscopically non-homogeneous precipitation process in beryllium-nickel alloys plays only a minor *rôle* in the hardening, coming into play only when most of the new phase has been precipitated. The black zone in the etched specimens is due chiefly to coagulation of the disperse phase, which primarily separates by microscopically homogeneous precipitation.

The Corrosion of the Tin-plate Container by Food Products.

By T. P. HOAR, M.A., Ph.D.*

Two reports by T. N. Morris and J. M. Bryan[1] on the corrosion of cans by food products deserve study by metallurgists interested in tin-plate and other canning materials, not less so because the authors have approached the problem from the canning rather than the metallurgical point of view. The first report begins with a survey of the very diverse work carried out in this field up to 1930, which is mainly of American origin. Investigations of the factors influencing the attack of tin and steel by weak acid media between pH 2 and pH 6 (the outside pH limits of canned fruits) are then described, and the very complex nature of the interacting factors becomes evident. The second report much extends the work, and also describes a number of experiments with aluminium cans. The present article is intended to give a brief critical summary of the work and the conclusions reached, especially those of more direct metallurgical interest.

The thin layer of tin covering the steel-base of ordinary tin-plate always contains pores, and the deformation of the material in fabrication produces further discontinuities in the coating. For this reason all studies of tin-plate corrosion must take account of the corrosion of both tin and the underlying steel. The greatest amount of trouble found in practice concerns acid foodstuffs, such as fruits, which sometimes give rise to swollen cans, owing to the evolution of hydrogen, and in extreme cases to perforation owing to metal dissolution. Thus Morris and Bryan have chiefly studied the corrosion of tin and steel under conditions of weak acid attack. Dilute citric acid, buffered to different pH values with sodium citrate, was used as a standard simple solution, but the influence of numerous additions likely to be present under practical fruit-canning conditions, such as cane sugar, beet sugar, pectin, traces of sulphur, &c., were carefully investigated. A number of practical canning tests with various fruits and corrosion tests with actual fruit extracts were also carried out.

The corrosion of tin by weak acids has long been thought to be practically negligible in the absence of air, and Morris and Bryan find complete confirmation of this view. When air is present, however, considerable attack may take place in acids such as citric, malic, lactic, and tartaric, whereas acetic acid has little corrosive action. It is suggested in the second report that, apart from oxalic acid, only acids containing a hydroxy-group can attack tin under these conditions. This conclusion seems too sweeping, for in hitherto unpublished work I have found that the non-hydroxy formic, maleic, and chloracetic acids attack tin more rapidly than citric acid. Nevertheless, it is probably true to say that all hydroxy-acids give rise to attack, though they are not alone among organic acids in so doing.

The increase of pH obtained by the addition of sodium citrate to citric acid leads to a general decrease of the rate of attack,[2] both at 25 deg. and 75 deg. Cent. Small quantities, *e.g.*, 20 parts per million, of iron or copper slightly accelerate the attack, while 25 per cent. sucrose considerably retards it at 25 deg. Cent., giving, however, acceleration at 75 deg. Cent. In general, increase of sugar content of the acid liquor decreases attack at the lower temperature; 1 per cent. sodium chloride has no influence except for a slight retardation in the high pH solutions.

The composition of the tin has a small influence on its rate of attack by citric acid. The presence of small amounts of antimony or bismuth, up to 0·5 per cent., gives a retardation of the rate of attack of some 10–20 per cent., as compared with the pure metal. Further increase in the amounts of antimony or bismuth gives no greater effect. The antimony content of tin which is to be in contact with foodstuffs must, of course, be kept low.

The corrosion of steel of the type used for tin-plate steel-base is more complicated than that of tin. In dilute weak acids, it occurs readily in the absence of air, though it is somewhat accelerated by the presence of air, especially in the higher pH liquids studied, *e.g.*, pH 4–5. An important feature of the first report is the clear demonstration of the great differences in the rate of attack of different samples of steel-base. These differences are the most marked in the most acid solutions; moreover, a steel which is at pH 2·5 "fast" compared with another, may often become actually "slow" compared with the second at a pH greater than about 4·5. The second report accepts the conclusion of Hoar and Havenhand,[3] whose work arose out of the first, that one factor producing acceleration of weak acid attack is the presence in mild steel of sulphides soluble in weak acids. This hypothesis is strongly supported by the known influence of a few parts per million of hydrogen sulphide or sulphur dioxide in much accelerating the attack of "slow" steels at pH 2–3, while often giving retardation above pH 4·5. Hoar and Havenhand use electro-chemical evidence to explain the accelerating influence of traces of hydrogen sulphide in acid solution as due to stimulation of the sluggish anodic reaction $Fe \longrightarrow Fe^{++} + 2\varepsilon$. Morris and Bryan suggest that the retarding influence above pH 4·5 may be due to the formation of a ferrous sulphide film, but it is more likely due to an inhibition of the oxygen depolarisation cathodic reaction predominant at this pH.

The influence of other constituents in the steel-base on its attack by weak acids is discussed in the second report with regard to the work of Hoar and Havenhand, which was directed more specifically towards this question. Morris and Bryan point out that the accelerating influence which some authors have attributed to phosphorus may be, certainly in part, really that of sulphur, since the percentages of these elements in ordinary mild steel and tin-plate run closely parallel. It may be noted that the results of Hoar and Havenhand give no evidence for any direct

* Research Investigator, International Tin Research and Development Council.

influence of phosphorus. These authors, however, present considerable evidence for the view that small amounts of copper in the steel counteract the accelerating influence of sulphur under conditions of weak acid attack.

Tartaric, malic, and acetic acids are shown by Morris and Bryan to give attack on steel very similar to that found in citric acid; however, oxalic acid behaves differently.

Steel is much less rapidly attacked in solutions of higher pH obtained by buffering citric acid with sodium citrate,[4] the effect being the most marked for those steels which are "fastest" in the more acid solutions. Considerable retardation of the attack by citric acid is effected by a few parts per million of tin ions,[5] or small amounts of gelatin. The effect is greatest at low pH, becoming small at pH 5 and greater for "fast" steels than for "slow"; 25 per cent. sucrose reduces the attack over the whole pH range (2–6) studied, but interferes somewhat with any simultaneous inhibition by tin ions. Beet sugar is especially effective in reducing attack, undoubtedly because it contains a small quantity of a potent inhibitor. Pectin, starch, and other colloids give a moderate degree of inhibition.

The corrosion of steel by fruit extracts is evidently still more complicated than that by simple weak acid solutions, on account of the numerous inhibitory and accelerating substances present. Morris and Bryan show that there is a clear parallel between the rate of attack of steel-base in a number of fruit extracts under laboratory conditions and the actual rate of failure of cans of similar fruits packed in similar tin-plate. Also, addition of citric acid to the less acid fruits, such as cherries, is shown to reduce attack of steel-base by cherry extract under laboratory conditions and to reduce the incidence of hydrogen swells in canning experiments, probably because the inhibitors present are more effective at the lower pH. It is clear, however, that the relative importance in practice of the various factors concerned with the composition of the steel-base and of the fruit juice can only be settled by practical canning experiments covering a wide range of tin-plate, as it is normally obtained, and using as many types of fruit as possible.

Since tin and steel occur in galvanic couple at pores in tin-plate exposed to an electrolyte, Morris and Bryan have studied the corrosion of the metals in couple under simplified conditions. The important general conclusion that relatively rapid corrosion of one metal is nearly always associated with relatively slow attack of the other is of interest. This phenomenon is partly due to the flow of current in the tin-steel couple. If the tin is anodic towards steel (its usual condition in citric and similar acids), coupling of the metals tends to increase the attack on the tin by anodic dissolution but to decrease that on the steel by cathodic protection. In cases where steel is anodic (for instance, when considerable sulphur is present or in acetate solutions which scarcely attack the tin), the reverse is true. Another contributory cause of the phenomenon is the strong inhibiting influence of dissolved tin ions on the steel attack; evidently greater attack on tin leads to less on the steel.

The well-known diffusion of hydrogen through steel during acid attack is clearly important from the point of view of hydrogen swells. The second report considerably extends our knowledge in this field, with regard to citric acid attack.[6] It is found that traces of reducible sulphur greatly enhance hydrogen diffusion, and that "fast" steels, presumably because of their higher sulphide content, give a greater ratio of diffused hydrogen to evolved hydrogen than do "slow." It should be noted that this effect may modify the parallel (to be expected on general grounds) between the rate of attack of steel-base under laboratory conditions and the actual rate of hydrogen swell formation in cans. Gelatin (and probably other similar inhibitors of acid attack) retards both the diffusion and evolution of hydrogen about equally. This and other evidence leads to the view that such bodies inhibit the reaction $H^+ + \varepsilon \longrightarrow H$ rather than $H + H \longrightarrow H_2$. Morris and Bryan observed, but do not explain, the rather remarkable fact that a tin coating on the dry side of steel sheet undergoing acid attack on the other, almost entirely prevents hydrogen diffusion. This is probably because the diffusing hydrogen atoms, which can combine to form molecules at an iron-air interface, cannot do so at the iron-$FeSn_2$ interface, nor can they diffuse through the $FeSn_2$ layer. A coating of lacquer, however, offers no impediment to the diffusion.

The canning-tests so far reported indicate the advantage of additions of citric acid to some of the less acid fruits, especially those which, owing to their anthocyanin colour, have to be packed in lacquered cans, which are known to be more prone to hydrogen swells than are plain cans. The citric acid addition much diminishes the incidence of hydrogen swells. The advantages of cans sprayed with lacquer after fabrication are also exemplified, and it is suggested that if perfect lacquer coatings could be devised most can corrosion problems would be solved. Better methods of tin-plate manufacture leading to more nearly perfect tin coatings, which will incidentally give more effective lacquering, and improvements in can fabrication are advocated, the production of cans with both lacquer and tin coatings as little damaged as possible being always the end in view.

Aluminium cans, while satisfactory for fish and other nearly neutral foods, were found by Morris and Bryan to be unsuitable for acid fruit products, owing to the relatively rapid formation of hydrogen swells and discolouration of the fruit. Spray-lacquered aluminium cans gave quite good results, but it is pointed out that these were stored under very favourable conditions, without any rough handling, such as a commercial product might well undergo, which would be expected to damage the lacquer coating and lead to rapid failure.

Other matters dealt with in the reports include the discolouration of canned fruits by metallic contamination, the cooling of cans after processing, and cool storage.

It may be pointed out, in conclusion, that the two reports here reviewed are themselves summarised versions of a series of papers published in the annual reports of the Food Investigation Board for 1928 onwards. Reference to the more detailed papers may be found in the special reports.

References.

[1] T. N. Morris and J. M. Bryan, Food Investigation Specia Report, No. 40, 1931; Special Report, No. 44, 1936. H.M. Stationery Office, London.

[2] J. M. Bryan, Trans. Faraday Soc., 1931, 27, 606.

[3] T. P. Hoar and D. Havenhand, J. Iron and Steel Inst., 1936, 133, 239P.

[4] J. M. Bryan, Trans. Faraday Soc., 1933, 29, 1198.

[5] T. N. Morris and J. M. Bryan, Trans. Faraday Soc., 1933, 29, 395.

[6] T. N. Morris, J. Soc. Chem. Ind., 1935, 54, 7T.

Books and Publications.

Tungsten: A Treatise on its Metallurgy, Properties, and Applications. By COLIN J. SMITHELLS. Second edition, revised. Royal 8vo. Pp. viii +272. 1936. London: Chapman and Hall, Ltd. 25s.

SINCE the publication of the first edition of this book, Dr. Smithells has been widely recognised as the foremost authority on tungsten. By his continuous contact with the technical problems involved in the manufacture and utilisation of tungsten, his close acquaintance with the literature of the subject, and last, but not least, by his own original researches on the metal, Dr. Smithells has produced a thoroughly complete and up-to-date treatise on the subject.

The progress of the last ten years is reflected in the enlargement which the book has undergone. The chapters on the preparation, purification, and reduction of tungstic oxide, and on the manufacture of ductile tungsten have been amplified, and the discussion of the metallography of tungsten contains new matter, but the sections dealing with the effect of cold work and annealing on physical properties, and the properties of tungsten as a function of the temperature show a greater change.* New determinations of the physical properties of tungsten over a wide range of temperature have made available much more accurate data, the reliability of which has been ensured in many cases by interchange between the national standardising laboratories of Europe and America.

The field has become so large that Dr. Smithells has thought it well to call in the aid of expert help in some specialised directions. Thus Dr. A. L. Reimann contributes a chapter on "Thermionic Properties of Tungsten" and Mr. T. R. Bird another on the "Hard Alloys of Tungsten Carbide."

By far the greater part of the tungsten produced finds its way into steel and that mainly into steels for tools and dies with a subsidiary amount going into magnets and into valves for internal combustion engines. It is useful therefore to have under the same cover a review of "Tungsten-Iron Alloys and Tungsten Steels," by Mr. J. H. G. Monypenny.

In metallurgy the high melting point and high density of tungsten render it unique among the more readily available metals. The number of elements with which it forms alloys is not large and its high melting point militates against the facility with which it can be alloyed, but an important type of materials which receive mention in the book are the sintered "alloys"—materials which are not alloys in the strict sense of the term, but intimate mixtures of tungsten with another metal or with an alloy.† An instance of this is the "heavy alloy" containing tungsten with 5 per cent. of nickel and 5 per cent. of copper, sintered in hydrogen at 1350–1450 deg. Cent. This has a density of 17 and a tensile strength of 22 tons per square inch. It was developed by Dr. Smithells primarily for radium bombs as a substitute for lead (density 11·3), but alloys made on this principle have also been used for balancing crankshafts for internal combustion engines used in racing motor cars and in gyroscopes. The 10 per cent. copper tungsten sintered alloy sold under the name of "Elkonite" is used in the form of a facing brazed on to copper contact arms, as a contact material for heavy current circuit breakers.

The metal tungsten is the immediate concern of relatively few specialists engaged in the industry, but it has a wide general interest in metallurgy and in physics. Dr. Smithells' book is written and produced in a manner admirably adapted to meet the needs not only of the tungsten specialist and of the scientific investigator in other fields, but of the larger class of reader drawn from the users or potential users of tungsten products.

The Alloys of Iron and Carbon: Vol. II, Properties. By FRANK T. SISCO. 8vo. Pp. xiii+777. New York and London: McGraw-Hill Publishing Company, Ltd. 1937. 45s.

THIS latest addition to the monographs published under the auspices of the Iron Alloys Committee of the Engineering Foundation of America is a continuation of the volume on the "Constitution of the Alloys of Iron and Carbon," by S. Epstein. It deals with variables affecting the properties of steel castings, the mechanical properties of cast steel, hot-worked, cold-worked, and heat-treated carbon steels, and the effect of cross section and other variables on mechanical properties. The next three chapters of the book refer to cast iron, and then follow seven chapters dealing with the properties of carbon steels as revealed by certain specialised tests, such as fatigue tests and high-temperature tests of all kinds, together with measurements of corrosion resistance, physical properties of all kinds, including electrical and magnetic properties, and miscellaneous information of engineering importance relating to damping, deep-drawing, machinability, weldability, and wear resistance.

Mr. Sisco has had, in one respect, a more difficult task than any of the authors of other books in this series. The extent of the literature on the properties of carbon steels is enormous, and a large amount of it consists of direct duplication and restatement of reported facts. After careful sifting it was found impossible, on account of the necessary restriction of space, to include abstracts of or references to all papers which have some claim to be considered important. This, however, does not detract from the value of the author's considered opinion on each section of the subject, which, as in other books in this series, forms an exceptionally valuable conclusion to each chapter.

In dealing with the large volume of data available for defining the properties of carbon steels, Mr. Sisco advocates the importance of statistical analysis. Almost every factor in the production of a finished steel section is subject to variations, and these variations affect the properties to a greater or less degree. Apart from a few physical constants which can be given in absolute values, most of the important engineering properties can only be stated as an approximation. Statistical methods enable the accuracy of the approximation to be assessed and give important information on the character of the variables present, whether they are or are not beyond the control of the investigator. The subject can readily be pursued by the aid of the references given in the book.*

Mr. Sisco's critical summary of the properties of carbon steels will take a high place among the Alloys of Iron Research Monographs, and indeed is an indispensable member of the series, since, together with Vol. I on Constitution, it provides the necessary "base line" with which the properties of alloy steels may be compared.

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* But Kelvin's surname still retains the superfluous *p*.

† An account of these sintered alloys is given by Dr. Smithells in *Nature*, March 20th, 1937, page 490.

* Or in Dr. T. P. Hoar's article on the subject, THE METALLURGIST, June, 1936, 10, 134.